Effect of EOR Surfactant on Reservoir Rock Wettability

By

Amir Safwan Bin Shuib

8128

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

ACKNOWLEDGEMENT

To my mother

I would like to thank my supervisor, Mr Ali of Geoscience and Petroleum Engineering Department for his enthusiasm and keen interest in my works. His wisdom has let me better understand the concept of relative permeability, the effects of wettability change to relative permeability and the complexity of the experiment. His experience has led me to discover a simpler and better method to measure a change in wettability that is contact angle measurement using an IFT device. I then explored the device different functions and abilities; pendant drop, sessile up, and sessile down orientations. I am very thrilled to know that I am the first in UTP to use the sessile up setup of the IFT 700 device. Being a pioneer means the learning curve is steep as there are a lot of never-seen-before problems to be encountered and solved in order to complete the experiment. I owe this exciting experience to Mr Ali.

I would also like to thank the most helpful technician I know, Mr Rizuan of the Core Analysis Lab, Petroleum Engineering Department for without his tireless assistance, the experiment cannot be performed. His presence is also to ensure everyone's safety as the device pressure regulator uses high pressure to fill the brine/surfactant up the test chamber. I have learned so much while working with him especially in solving the mechanical and operational problems while using the IFT 700.

I think this next person also deserve credit eventhough he is not directly involve with my project, Mr Idris, researcher/ PhD student. He has shown a great interest in my experiment. I'm thanking him for explaining the Young's equation in details and how the equation can be manipulated to give a representation of wettability. He also emphasized the important of filling the test chamber with the same fluid used to saturate a core slice. He manage to oversee my works in between his research work on relative permeability as we share the same lab.

Advices, assistance, guidance, and support from the following are also highly appreciated; Ms Faiza (FYP 1 supervisor, Geoscience and Petroleum Engineering), Dr Isa Tan (Lecturer, Chemical Engineering), Murshid (Postgraduate student), lab executives and technicians of both Chemical Engineering and Geoscience & Petroleum Engineering Departments, family and friends.

ABSTRACT

The use of surfactant is proposed as one of the methods to enhance the oil recovery from reservoir whereby the conventional methods such as waterflood and production by natural drive are no longer sufficient to produce the remaining oil. Primarily the ability of surfactant to reduce the oil-water interfacial tension and alter the reservoir wettability making it a viable option being explored today. IFT reduction will increase the oil mobility thus contributing for greater oil recovery. Wettability alteration from oil wet to water wet or less oil wet will improve water imbibition. This study focus on the effect of surfactant concentrations on reservoir rock wettability (contact angle). Synthetic brine (Sodium Chloride, 1500ppm), crude oil (Baronia) and an ionic surfactant (Sodium Dodecyl Sulfate, 0, 500, 1500, 3000 and 5000ppm) have been used in this study. Sessile up or bubble technique has been used to obtain the contact angle. A high speed magnifying camera produced a live video feed that enable image capture of the oil bubble for contact angle analysis. The contact angle is found to increase from 40.36° to 52.59° for the test with 0 ppm and 500 ppm surfactant respectively. This change of wettability to less water wet condition is discussed in the result and discussion sections. The experiment is repeated for the 500 ppm and 1500 ppm surfactant concentration where the contact angles were found to decrease from 40.24° to 25.20° respectively.

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Universiti Teknologi PETRONAS
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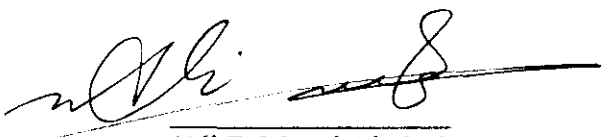
Approved by,



(Ali F. Mangi Alta'ee)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AMIR SAFWAN BIN SHUIB

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CHAPTER 1

1. INTRODUCTION/PROJECT BACKGROUND

1.1. Background

Wettability is defined as the "tendency of one fluid to spread on or adhere to solid surface in the presence of other immicible fluids". (Tarek Ahmad, 2001) Wetting always usually involves three phases. The possible combinations of phases are; a gas and two immicible liquids, or a solid and two immicible liquids, or a gas, a liquid and a solid, or three immicible liquids [27].

Resevoirs wettability varies from fully water wet to fully oil wet. For a fully water wet reservoir, water occupies the small pores and most of the rock surface is in contact with water. When the rock has no strong preference for either oil or water then it is an intermediate or neutrally wet reservoir. In a fully oil wet reservoir, oil covers most of the rock surface and small pores. There are also reservoirs with fractional wettability also known as heterogeneous, spotted or dalmation [4].

There are various methods exist to measure wettability. Examples of qualitative wettability measurements are imbibition rates, microscope examination, flotation test, relative permeability curves, reservoir logs, nuclear magnetic resonance (NMR), and dye adsorption. Contact angle measurement, Amott method and United States Bureau of Mines, USBM method represent quantitative methods of wettability measurement. Amott and USBM methods are widely acceptable quantifiying method in the industry.

Surfactant comes from the term *surface-active agent.* The uses of surfactant are very diverse ranging from motor oil in automobiles, detergent and pharmaceuticals. Among its high potential uses that is being explored now is the use of surfactant in enhance oil recovery (EOR). It has the ability to reduce interfacial tension (IFT) and altering wettability.

1.2. Problem Statement

1.2.1. Problem Identification and Significant of the Project

Dwindling discoveries of new oil fields and increasing demand for oil have forced the excercise of studying the various alternatives methods proposed to recover the remaining or residual oil from mature fields [1,2]. Conventionally waterflood or gas injection are being used to maintain an economic production when the primary drives are exhausted [1]. Waterflood, however is not always effective especially in oil wet or fractured carbonate reservoirs.

Generally only one-third of oil originally in place (OOIP) can be recovered economically using the existing technology such as primary recovery methods that utilize gas pressure and pressure depletion and secondary recovery method using waterflood [6,9]. The remaining 50-70% of oil can only be removed with enhance oil recovery (EOR) methods such as; using chemical, thermal or gas injection [1].

Market study shows that, about 60% of the world's oil and 40% of the world's gas reserve are in the carbonate reservoirs [2]. There are huge potential for implemetation of EOR methods, especially in the middle east [1]. Large portion of the middle east reserves are located in carbonate reservoirs; table 1 [6].

Table 1. Middle East Oil and Gas Reserves [6]

	Oil	Gas
Middle East world's reserve	62	40
Middle East reserves in carbonates	70	90

However recovering oil from carbonate reservoir present certain challenges. The recovery from sandstone reservoir is always higher than carbonate reservoirs [2]. Complex depositional history and diagenesis action over time created heterogeneity in the pores, grain and texture of carbonate reservoirs [2]. Most of carbonate reservoir are heavily fractured, or mix-wet to

oil-wet or both making recovery using waterflood very low [1,9]. Residual oil saturation at the water invaded region remains high in fractured, oil-wet, carbonate formation [1,5]. The residual oil is trapped due to capillary effect, high interfacial tension (IFT), unfavourable wettability and effect of diagenesis on rock permeability.

Trapped oil in fractured, oil-wet, carbonate reservoir can be recovered by promoting spontaneous imbibition. There has been considerable effort to study surfactant ability to promote spontaneous imbibition in order to recover the trapped oil [5,7]. Spontaneous imbibition can be enhanced by adding surfactant into the injected water. Interfacial tension (IFT) reduction and wettability alteration have been determined as the mechanisms that promote spontaneous imbibition enhancement [1,5,6,7,8,9].

Surfactant can be used to create ultra low IFT between surfactant bank and residual oil thus increase the trapped oil mobility [7]. However, several orders of magnitude reduction in IFT is required for significant oil recovery [25]. This requires the use of surfactant in large quantities. The surfactants with the ability to reduce IFT are expensive [25]. On the other hand, low cost surfactant can be used at moderate concentration to alter wettability from oil-wet to mix/water-wet [25]. This study will look into both the IFT and wettability alteration ability of the surfactant.

1.2.2. Objectives and Scope of Study

The scope of this study is limited to the surfactant ability to alter wettability. The objective of this study is;

- To discern the effect of surfactant concentrations on reservoir rock wettability.

CHAPTER 2

2. LITERATURE REVIEW

2.1. Studies on Wettability Alteration using Surfactant by IFT and/or Contact Angle Measurement

Chandra S. Vijapurapu *et al.* (2003) performed an experimental work to study the effect of brine dillution and surfactant addition on spreading and adhesion behaviour Yates crude oil on dolomite surfaces [23]. Oil-water IFT and dynamic (water advancing and receding) contact angles are measure using Computerized Axisymetric Drop Shape Analysis (CASDA) technique and Dual-Drop-Dual-Crystal (DDDC) technique respectively. Yates reservoir brine was mixed with deionized water (DIW) in various proportions for the brine dilution study. Oil-water IFT was found to decrease initially with decreasing volume percent of brine in the mixture. Further dilution of reservoir brine results in increase of IFT. Water advancing contact angle was found to decrease with brine dilution changing the wettability from oil-wet to intermediately wet. Also, Ethoxy Alcohol surfactant was found to altered the wettability of Yates reservoir rock-fluids system wettability from strongly oil-wet to water-wet at concentration of 3500ppm by reducing the advancing angle from 158° to 39°.

Jingquan Li *et al.* (2004) used the axisymetric drop shape analysis (ASDA) technique for sessile drop case to study the dynamic interfacial tension (IFT) phenomenon and wettability alteration of crude oil-rock-alkaline-surfactant solutions systems [24]. Sodium hydroxide, NaOH solution of various concentrations (0.2, 0.4 and 0.8 wt%) were used to study dynamic IFT behaviour in alkaline solution. Minimum IFTs were observed at 8-20 seconds after NaOH addition. It is assumed that dynamic IFT is inversely proportional to interfacial concentration of the surfactants. Therefore the minimum IFTs attained are attributed to the maximum concentration of surfactant generated at the interface. The surfactants are generated in-situ by the chemical reaction between natural organic acids in the crude oil and the added alkali. Immediately after the crude oil made contact with alkaline solution, the generated surfactants will diffuse

into the aqueous phase and into the oilphase as well. It was observed that after the minimum IFT attained, the dynamic IFT starts to increase gradually. However, at low NaOH concentrations (0.2 and 0.4 wt%) the dynamic IFT increase until they reached the initial value. This was not observed at high NaOH concentration.

Jingquan Li *et al.* (2004) also in the same work found that the measured contact angle with time at 0.2, 0.4 and 0.8 wt% NaOH concentrations increase to maximum values then gradually decrease to initial values. This wettability alterations confirm with the dynamic IFTs [24]. The wettability first changed to more water wet then slowly reverse to initial conditions. Effect of alkaline-surfactant, AS solutions on wettability alteration were studied as well. Cationic surfactant-alkaline solution was found to change the wettability from initially water wet to oil wet. While anionic surfactant-alkaline increases the contact angle initially then decreases the contact angle gradually to a minimum, which shows that the wettability alteration is temporary.

W. Xu *et al.* (2005) studied the effect of surface active chemicals on oil-water interfacial tension (IFT) and wettability in crude oil-brine-rock systems at reservoir conditions [21]. Live and stocktank crude oils subjected to reservoir conditions were used to measure IFT and dynamic contact angle using Drop Shape Analysis (DSA) and Dual-Drop-Dual-Crystal (DDDC) respectively. Yates reservoir rock and fluids and two types of surfactants (nonionic and anionic) in varying concentrations were used in this study. The anionic surfactant used in the study was found to alter the wettability of the live oil system from water wet to intermediate wet. However it did not affect the strongly oil wet of the stocktank oil system.

Seethepalli *et al.* (2004) studied the interactions of dilute alkaline anionic surfactant solutions with crude oil on carbonate mineral surfaces [18]. Six anionic surfactants (SS-6656, Alfoterra 35, 38, 63, 65, 68) have been found to change the wetability of the calcite surface to intermediate/water-wet condition. West Texas crude oil was used in the study.

Shunhua Liu *et al.* (2008) conducted a laboratory study of the alkaline-surfactant-polymer (ASP) [19]. The results show that presence of sodium carbonate reduce the adsorption of anionic surfactants on carbonate surfaces. Also, optimal salinity for alkaline conditions was found to depend only on the soap-to-surfactant ratio for any system of synthetic surfacant and crude oil containing napthenic acids.

T. Babadagli (2003) studied oil recovery from different rock types to identify and analyze the recovery mechanisms due to capillary (sponteneous) imbibition of surfactant solution [20]. He used various types of rocks; sandstone, limestone, dolomitic limestone, and chalk. Oil phase were selected from a variety of oils too; light and heavy-crude oils, kerosene, and engine oil. Surfactant of different types (non-ionic, anionic) and concentrations were used as the aqueous phase. The study found that non-ionic surfactant solution increase the recovery rate and ultimate recovery of heavy-oil in water wet sandstone as compared to brine imbibition. The same surfactant also yield higher ultimate recovery and faster recovery rate in all cases studied except for light oil cases such as kerosene and light crude oil in sandstones. This is attributed to wettability alteration due to the addition of the surfactant.

Dandina N. Rao (1997) conducted a study in an attempt to compare the wettability derived from reproducible dual-drop-dual-crystal (DDDC) tests with wettability deduced from corresponding oil-water relative permeabilities of corefloods experiments [10]. The findings provide insight into understanding relationship between wettability obtained from both methods. Out of six case studies compared, four rock fluids systems yeild similar wettability from both corefloods and contact angle.

D. Leslie Zhang *et al.* (2006) investigated the controlling mechanisms and variables of improve oil recovery using surfactant [5]. Leslie found the use of alkaline/surfactant systems are able to alter wettability of calcite from intermediate-wet to water-wet. The presence of sodium carbonate also significantly reduce the anionic surfactant adsorption.

Mehdi Salehi *et al.* compared the effectiveness of a low cost surfactant obtained from high starch industrial and agricultural effluents known as anionic biosurfactant (surfactin) with the commercially available surfactant, STEOL CS-330 [7]. The study was conducted using crushed Larsing-Kansas City carbonates. The result shows surfactin is more effective than STEOL CS-330 in altering wettability from oil-wet to water-wet.

Stephen J. Johnson *et al.* performed a study intended to find the mechanisms that promote spontaneous imbibition by altering wettability from oil-wet to water-wet state [8]. The result of the study concludes that ion-pair formation and adsorption of surfactant molecules through interactions with the absorbed crude oil components on the rock surface as the main mechanisms that enable wettability alteration.

Yongfu Wu *et al.* (2006) studied the mechanism responsible for enhance oil recovery (EOR) from fractured carbonate reservoir through the use of surfactant [9]. This study also provide insight on quick screening method to find effective chemical formulations. Napthenic acid dissolved in decane is used to make calcite surface less water-wet. The result found that flotation test is a useful screening tool to identify better EOR surfactants for carbonates.

2.2. Surfactant

Surfactant molecular structure is generally divided into two main parts. The part that is repulsive towards solvent is known as *lyophobic group.* The other part which is very attractive towards the solvent is known as *lyophilic group.* If the solvent is water then both part are knowns as *hydrophobic* and *hydrophilic* respectively.

Surfactants are classified by their surface active portion charge;

1. Anionic (negative)
2. Cationic (positive)
3. Zwitterionic (both positive and negative are present)
4. Nonionic (no apparent ionic charge)

2.3. Wettability Measurement Methods Review

2.3.1. Contact Angle

Contact angle is one of the quantitative methods of wettability measurement. The different kinds of contact angle methods include; tilting plate method, sessile drops or bubbles, vertical rod method, tensiometric method, cylinder method, and capillary rise method [26].

The common methods of contact angle measurement employed in petroleum industry are sessile drop method and its modified form. Both methods require the mineral crystal to be tested is mounted in a contaminant free test cell made of inert material.

Sessile drop method only need a single flat, polished mineral crystals while the modified sessile drop method uses two of the mineral crystal. Quartz and calcite crystals are commonly used in place of sandstone and limestone respectively. Figure 1 shows the sessile drop measurement representation. Table 2 shows angles correspond to type of wettability.

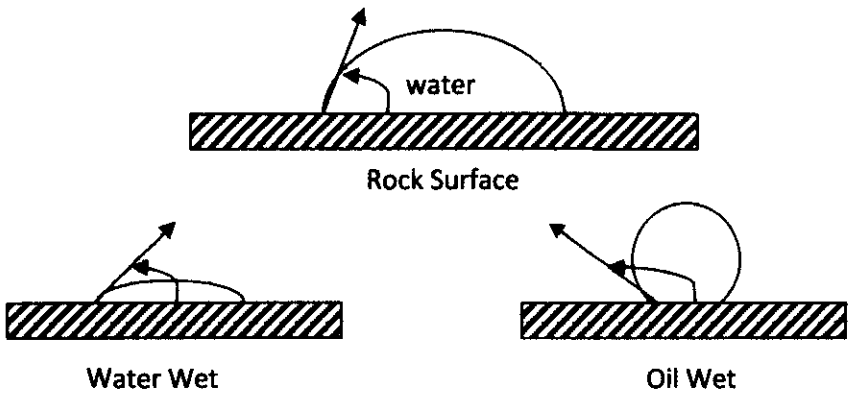


Figure 1. Contact Angle

Table 2. [26] Contact Angle Wettability Range

	Water-Wet	Neutrally-Wet	Oil-Wet
Minimum	0^{o}	$60\text{-}75^{o}$	$105\text{-}120^{o}$
Maximum	$60\text{-}75^{o}$	$105\text{-}120^{o}$	180^{o}

2.3.2. Amott Method

The Amott method combines spontaneous imbibition and forced displacement of fluids from a core to measure the average wettability of the solid surface. This method recognizes the fact that wetting fluid will generally imbibe spontaneously into a core, displacing the nonwetting fluid. The wetting fluid is forced to imbibe some more by using centrifuge.

The most important parameters to be measured in Amott method are;

1. Amount of water displaced by spontaneous imbibition of oil, $\mathbf{V_{wsp}}$
2. Amount of water displaced by force imbibition of oil, $\mathbf{V_{wt}}$
3. Amount of oil displaced by spontaneous imbibition of water, $\mathbf{V_{osp}}$
4. Amount of oil displaced by spontaneous imbibition of water, $\mathbf{V_{ot}}$

The parameters measured above are used in the following calculation of displacement by oil ratio δ_o and displacement by water ratio δ_w

$$\delta_o = \frac{V_{wsp}}{V_{wt}}$$

$$\delta_w = \frac{V_{osp}}{V_{ot}}$$

2.3.3. USBM Method

This method is developed by Donalson *et al.* (1969). Average wettability of the core is measured through centrifugal displacement. Wettability is calculated using the following formula;

$$WI = \log(A_1 / A_2)$$

Where A_1 and A_2 are areas under the oil and brine drive curves respectively.

2.4. Relative Permeability Measurements

2.4.1. Permeability: Theory

Permeability is defined as the ability of fluid to flow through a porous media. Absolute permeability is the permeability when there is only one phase of nonreactive fluid present. When there are more than one phase of fluids present, the flow of one fluid is affected by another fluid thus giving rise to **effective permeability** and **relative permeability** terms.

Two or three of these fluids often exist together in reservoir rock; water, oil, and gas. When two mobile fluids are present in the reservoir, the effective permeability of the rock to each fluid for a horizontal system are defined as;

$$k_{wp} = \frac{q_{wp}\mu_{wp}}{A} * \frac{dL}{dP_{wp}}, \quad k_{nwp} = \frac{q_{nwp}\mu_{nwp}}{A} * \frac{dL}{dP_{nwp}}$$

$$\text{and } P_c = P_{nwp} - P_{wp}$$

$A = area$

$L = length$

The subscript *wp* and *nwp* refer to wetting phase and nonwetting phase respectively.

Relative permeability is the ratio of the effective to the **absolute permeability.** When a rock contains two phases of displacing and displaced fluids, the **effective permeability** of displacing fluid is measured when there is no more production of the displaced fluid.

Effective Permeability to oil, $K_o = \frac{q_o \mu_o L}{A \Delta P_o} * 10^3 \, md$

Effective Permeability to water, $K_w = \frac{q_w \mu_w L}{A \Delta P_w} * 10^3 \, md$

Effective Permeability to gas, $K_g = \frac{q_g \mu_g L}{A \Delta P_g} * 10^3 \, md$

Relative Permebility to oil, $K_{rg} = \frac{K_o}{K_a}$

Relative Permebility to water, $K_{ro} = \frac{K_o}{K_a}$

Relative Permebility to gas, $K_{rw} = \frac{K_o}{K_a}$

2.4.2. Steady State Method

The following fluid flow balance forms the basis of steady state techniques;

$$(q_o + q_w + q_g)_{in} = (q_o + q_w + q_g)_{out}$$

And $(q_o)_{in} = (q_o)_{out}, (q_w)_{in} = (q_w)_{out}, (q_g)_{in} = (q_g)_{out}$

Steady state experimental procedure for oil and water system;

1. Oil and water input rate are adjusted to a desired water-oil ratio
2. The cumulative volumes of oil and water injected and produced are recorded as functions of time (every 5 minutes interval)
3. When the produced fluid has the same water-oil ratio as the injected fluid, steady state condition has been attained. Steady state condition is maintained for 10 minutes
4. The pressure drop across the system and the flow rates of oil and water are recorded
5. The relative permeabilities to oil and water are calculated from the data and physical dimensions of the sample
6. The saturations are calculated from the weight of the core sample knowing the pore volume and the densities of the fluids
7. The injection water-oil ratio is adjusted to another value and step 2 to 6 are repeated

Calculations;

Usually there will be accumulation or 'piling up' of wetting phase at the outflow end of a sample due to the capillary characteristic of a rock. The normal wetting phase is water. This condition is known as the 'end effect'. This 'end effect' can be eliminated or reduced by injecting the fluids at sufficiently high flow rates. Thus saturation distribution in the system is considered uniform and capillary pressure Pc=constant and dPc=0

From effective permeability equations for wetting and nonwetting fluids;

$$\frac{dL}{dp_{wp}} = \frac{dL}{dp_{nwp}} = \frac{dL}{dP}$$

Then, effective permeability equations for water and oil

$$K_w = \frac{q_w \mu_w}{A} * \frac{L}{\Delta P} \text{ and } K_o = \frac{q_o \mu_o}{A} * \frac{L}{\Delta P}$$

The relative permeabilities K_{ro} K_{rw} are;

$$K_{ro} = \frac{K_o}{K_a} \text{ and } K_{rw} = \frac{K_o}{K_a}$$

This method takes a very long time to achieve steady state for each water-oil ratio.

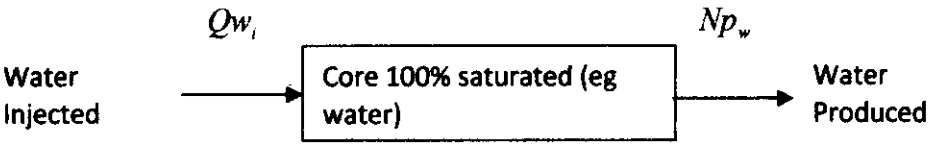
2.4.3. Unsteady State Method

The following fluid balance (water displacing oil) characterize the unsteady state method;

$$(q_w)_{in} = (q_w)_{out} + (q_o)_{out}$$

Relative permeability measurement;

1) Initial Condition



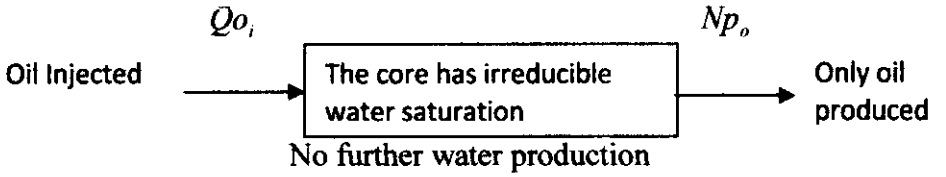
a. Absolute Permeability, (K_s):

$$K_s = \left(\frac{\Delta Q_w}{\Delta p}\right) \times \left(\frac{\mu_w L}{A}\right) \times 10^3 \, md$$

b. Pore Volume, (V_p):

$$V_p = \frac{W_s - W_d}{\rho_{sf}}, cc$$

2) Displacement (Displaced fluid by displacing fluid)



a. Initial Water Saturation, (Sw_r):

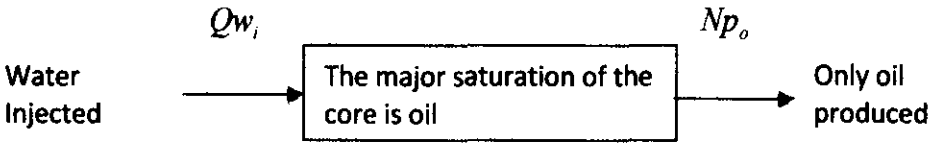
$$Sw_r = 1.0 - \frac{Cummulative\_water\_production}{Pore\_volume} = 1.0 - \frac{N_{wc}}{V_p}, fraction$$

b. Effective Permeability to Oil, (K_o):

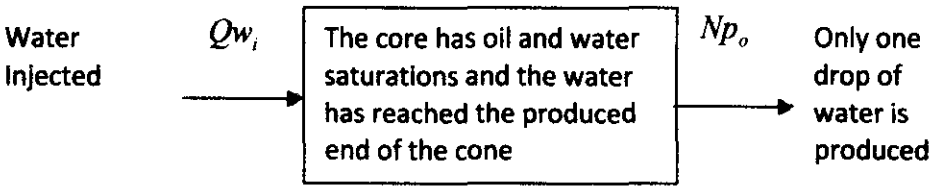
$$K_o = \frac{q_o \mu_o L}{A \Delta P_o} * 10^3 md$$

3) Relative Permeability Run

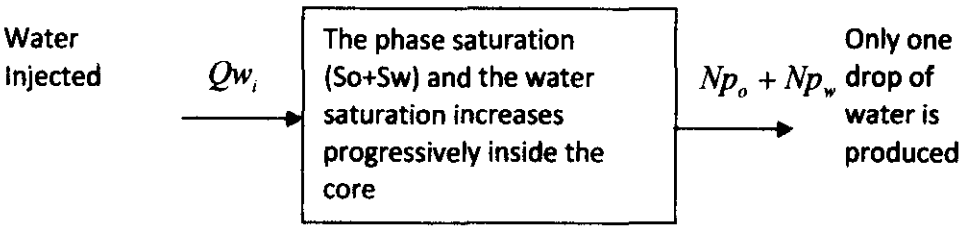
I. Before Breakthrough



II. At Breakthrough



III. After Breakthrough



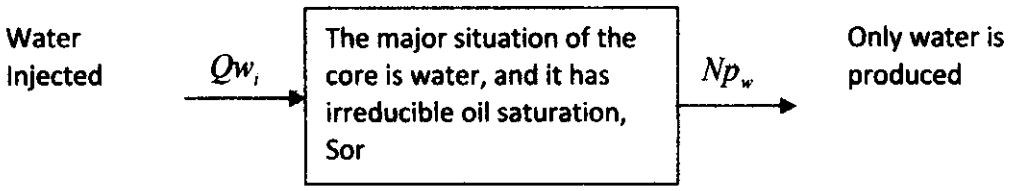
Ko and Kw at specified times are calculated together with the corresponding So and Sw using these equations;

$$K_{oi} = \frac{q_{oi} \mu_o L}{A \Delta P_{oi}} * 10^3 md \quad K_{wi} = \frac{q_{wi} \mu_w L}{A \Delta P_{wi}} * 10^3 md$$

$$S_{oi} = 1.0 - \left(S_{wr} + \frac{cummulativ\,oil\_volume\,produced at\_each\_period\_of\_time}{pore\_volume} \right)$$

$$S_{wi} = 1.0 - S_{oi}$$

IV. Abandonment Conditions



No further oil production

After completion of this stage, calculate residual oil saturation and the effective permeability to water using the following equations;

a) Residual oil saturation, (S_{or});

$$S_{or} = 1.0 - \left(S_{wi} + \frac{Cummulative\_oil\_produced}{Pore\_volume} \right)$$

$$S_{or} = 1.0 - \left(S_{wi} + \frac{NP_{oc}}{V_p} \right)$$

b) Effective permeability to water, (K_w);

$$K_w = \frac{q_w \mu_w L}{A \Delta P} * 10^3 \, md$$

2.5. Relative Permeability Interpretation using Craig's Rules of Thumb

"The wettability of a core will strongly affect its waterflood and relative permeability. Wettability affects relative permeability because it is a major factor in the control of the location, flow, and distribution of fluids in a porous medium" [16]. Craig's rules of thumb (Table 3) can be used to distinguish between strongly water-wet and oil-wet systems from relative permeability curves.

Table 3. Craig's Rules of Thumb

Parameters	Water-wet	Oil-wet
Connate water saturation, S_{wr}	20-25%< S_{wr}	S_{wr}<10%
Water saturation at which oil and water relative permeabilities are equal, $S_w@k_{rw}=k_{ro}$	50%< S_w	S_w<50%
Relative permeability to water at flood out, $k_{rw}@S_{or}$	k_{rw}<30%	50-100%< k_{rw}

2.6. Interfacial Tension (IFT) Relation to Contact Angle

Young equation below relates IFT and contact angle to each other for crude oil-water/brine-rock system. Figure 2shows the IFTs of the system.

$$\sigma_{OW}\cos\theta = \sigma_{SW} - \sigma_{SO}$$

Where;

σ_{OW} is crude oil-water interface tension

σ_{SW} is solid-water interface tension

σ_{SO} is solid-crude oil interface tension

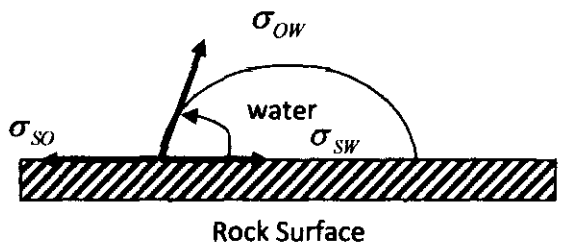


Figure 2. IFTs of crude oil-water/brine-rock system

2.7. Porosity Measurement (Boyle's Law)

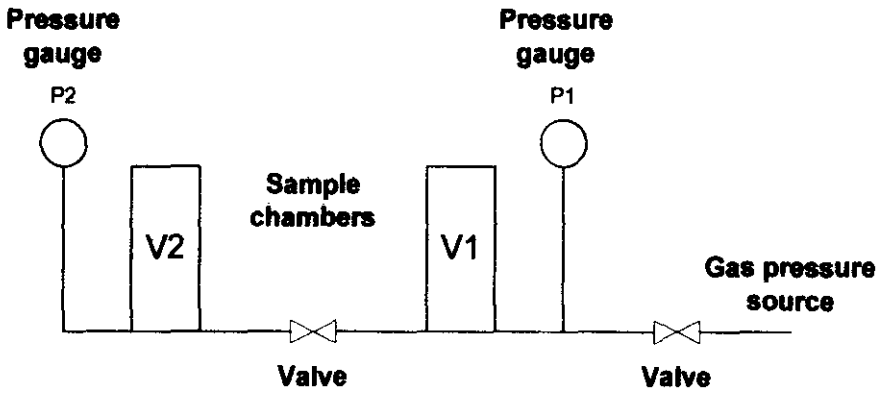


Figure 3. Schematic of a porosimeter based on Boyle's Law

A porosimeter uses helium gas as a pressurizing medium because it is not reactive and it has the smallest molecule size compared to other gases like nitrogen. At constant temperature, Boyle's Law states that product of pressure and volume subjected to condition 1 equals to product of pressure and volume subjected to condition 2.

$$P_1V_1=P_2V_2$$

The porosity measurement steps of a helium gas porosimeter;

1) Core sample is put in chamber 2
2) Helium is pumped into chamber 1 which has a volume of V1 and P1 is measured

3) Valve connecting chamber 1 and 2 is opened
4) P2 is measured after equilibrium
5) V2 can be calculated from Boyle's Law
6) Grain volume Vg=V1-V2
7) Pore volume Vpore=Vbulk-Vg
8) Porosity=Vpore/Vbulk

CHAPTER 3

3. METHODOLOGY

3.1. Reagents

The following reagents are used in this experiment;

a) Salt solution (brine) of 1500 from Chemical Engineering lab is prepared by dissolving sodium chloride, NaCl in distilled water.

Laboratory studies and field tests indicates that oil oil recovery can be improved with the use of low salinity brine [33, 34]. Salinity of less than 5000 ppm is normally implemented [33]. Properties of the injected water has been shown to affect the amount of oil recovered. Studies/research show consistent trend of higher oil recovery with lower brine salinity. Waterflood using low salinity brine has been shown to give better oil recovery than seawater injection or high salinity produced water injection [33].

P.L. McGuire *et al.* (2005) compare the oil recovery from the use of formation brine (15000 ppm TDS) and low salinity brine (1500 ppm TDS) [33]. The experiment was conducted using berea sandstone, crude oil and formation brine from BP-operated North Sea field (BPNS2). The result shows, the flooding with formation brine (15000 ppm) give 56% recovery of OOIP while the flooding with low salinity brine (1500 ppm) give 64% recovery of OOIP.

Y. Zhang *et al.* (2007) performed an experiment to study the effect of brine concentration on oil recovery [35]. Two consolidated reservoir cores of 600 md permeability each were injected with brines of 29690 ppm TDS and 1479 ppm TDS concentrations. Displacement tests showed that the recovery of OOIP from low salinity brine (1479 ppm) is 7 to 14% higher that from high salinity brine injection (29690 ppm)

b) **Baronia** Crude Oil supplied by Core Analysis Lab.

c) Ionic surfactant (Sodium Dodecyl Sulfate) supplied by Chemical Engineering lab.

Sodium Dodecyl Sulfate is dissolved in brine according to amounts listed in table 6 to form solutions of different concentrations (0ppm, 500ppm, 1500ppm and 3500ppm). This range of concentration is chosen because it is used in the field operations [25].

Numerous studies use the same range of concentrations in their experiments. For example, W. Xu *et al.* (2005) diluted ethoxy alcohol (nonionic surfactant) and ethoxy sulfate (anionic surfactant) each at the concentrations of 500ppm, 1500ppm and 3500ppm for their study [21]. Chandra S. Vijapurapu and Dandina N. Rao (2003) used surfactant concentrations of 0ppm, 50ppm, 100ppm, 1000ppm and 3500ppm in their experiment [23].

d) One sandstone core sample.

Berea Sandstone core sample (refer table 4 for core properties) is sliced to provide surfaces for the contact angle and IFT measurements. Berea sandstone is widely **recognized by the petroleum industry** since the past 30 years for the purpose of studying chemical surfactant efficiency [32].

Berea Sandstone is a sedimentary rock with predominantly sand-sized particles. It is composed of mainly quartz sand held together by silica. The core samples generally have high porosity and permeability which make it a good reservoir rock. Table 4 shows the chemical composition of Berea Sandstone™

Table 4. Chemical Composition of Berea Sandstone™

Mineral	Composition, %
Silica, SiO_2	93.13
Alumina, Al_2O_3	3.86
Ferric Oxide, Fe_2O_3	0.11
Magnesium Oxide, MgO	0.25
Calcium Oxide, CaO	0.10

Among the advantages of using berea sandstone as the test material of choice is its **excellent and uniform material properties**. Berea core samples has been **used by researchers around the world** to perform thousands core flooding tests for oil production characterization in other sandstone reservoirs during primary, secondary and tertiary oil flooding.

Researchers also are able to **compare their results** with numerous published findings in literatures and optimize their own processes. The following researchers (to name a few) also used berea sandstone in their studies; Sophany *et al.* (1977), S.M. Ma *et al.* (1999).

Table 5. Summary of Berea Sandstone advantages

Advantages of Berea Sandstone
• Recognized by the petroleum industry since 30 years for testing the effectiveness of surfactant • Good reservoir rock characteristic; high porosity and permeability • Uniform material properties • Widely used by researchers worldwide • Enable comparisons of results from published literatures

3.2. Saturation Duration

All the four core slices are saturated in the brine of different Sodium Dodecyl Sulfate concentrations (0ppm, 500ppm, 1500ppm, 3500ppm) for 15 days. The first three hours of the saturation is performed in a vacuum chamber. The saturation duration of published studies of surfactant effect on rock wettability, range from **one day** to **ten days.**

A. Seethepali *et al.* (2004) equilibrated the polished mineral plates with synthetic brine for **a day** [18]. The experiment was performed in order to study the wettability alteration caused by surfactant flooding on carbonate reservoirs. D. Leslie Zhang *et al.* (2006) equilibrated the polished and solvent cleaned marble plates with 0.1 M NaCl for **a day** [5]. They studied the wettability alteration and spontaneous imbibition in oil-wet carbonate formations caused by different surfactant concentrations, electrolyte concentration, etc.

Y. Zhang *et al.* (2007) performed a study on wettability characterization from spontaneous imbibition measurements [14]. They saturated the core sample with brine and let them equilibrate for **ten days.** Chandra S. Vijapurapu and Dandina N. Rao (2003) also studied the effect of surfactant concentration wettability [23]. In this experiment, two rock crystals were saturated with brine and left to equilibrate. However the equilibrating duration is not mentioned.

3.3. Wettability Measurement Technique Selection (Contact Angle and IFT)

Changes in wettability affect electrical properties, capillary pressure, waterflood behaviour, relative permeability, dispersion, etc. Therefore there can be a wide range of methods to measure wettability changes representation. Figure 4 on the next page show the various wettability measurement techniques screened to get the most suitable method, namely the contact angle measurement. The selection is made using the following criteria;

1) Industry standard, i.e method commonly used in Petroleum Engineering.
2) Availability of the necessary devices in UTP.
3) Time constrain. A time consuming technique is definitely not suitable for Final Year Project scale.
4) Limitations of the technique

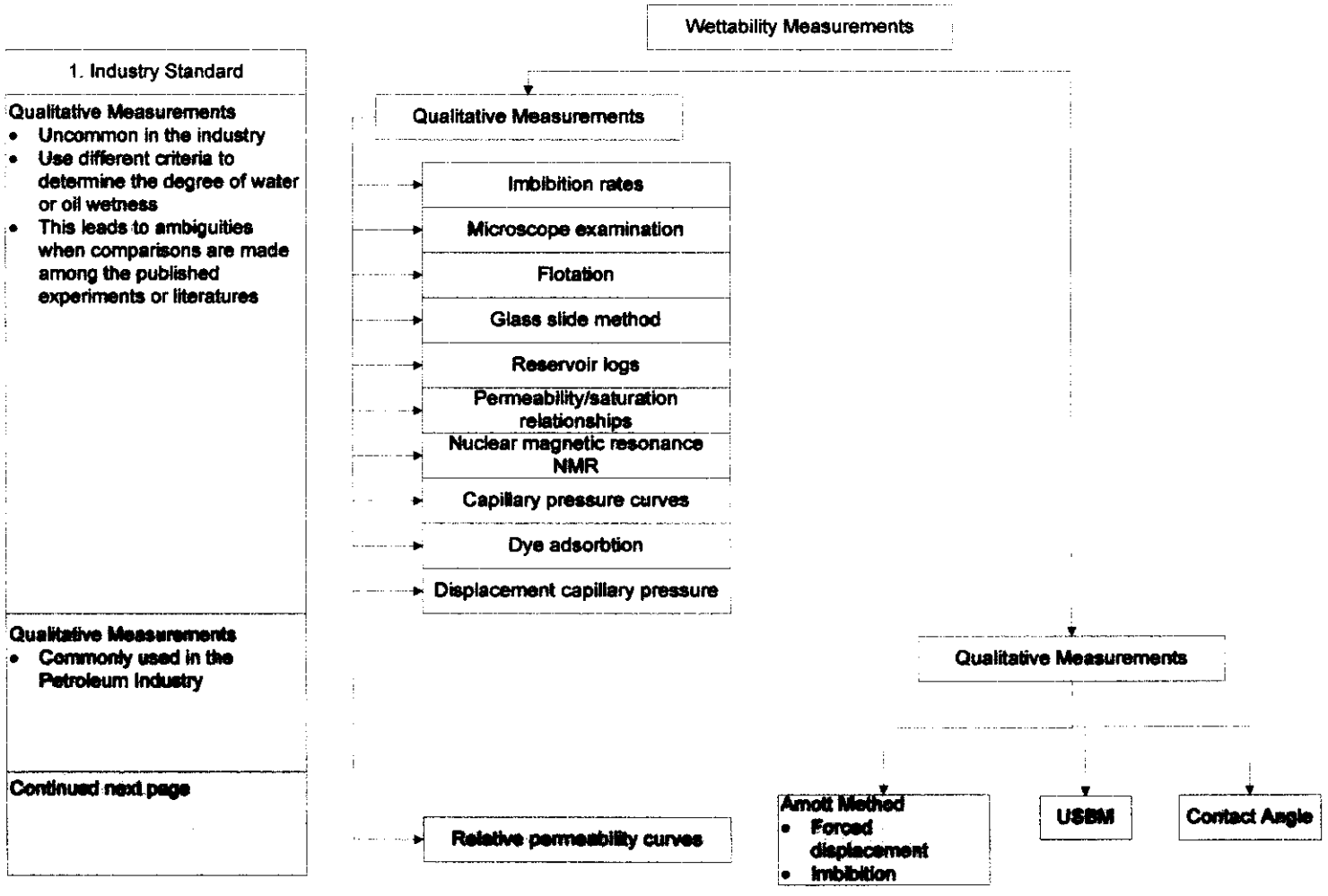


Figure 4. Wettability Measurement Technique Selection (continued next page)

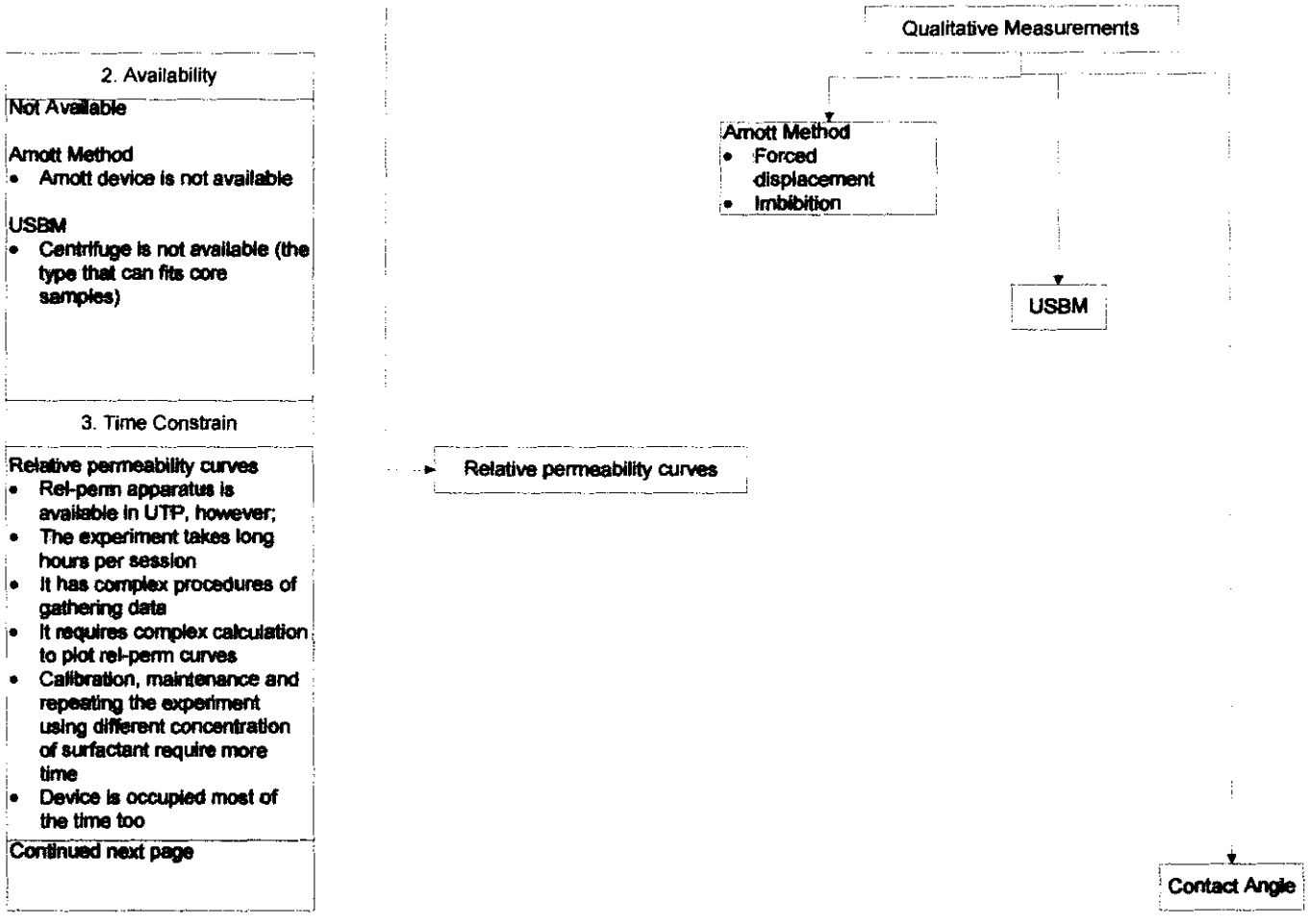


Figure 4. Wettability Measurement Technique Selection (continued next page)

These contact angle methods are not generally used in the Petroleum Industry

IFT 700 device available in Core Analysis Lab is able to support;

- Pendant Drop (liquid/vapor)
- Sessile Drop (VLS or LLS)

Sessile Up orientation is used in this experiment. See section **3.3.4. Contact Angle Measurement Procedure** for elaboration on sessile down and sessile up.

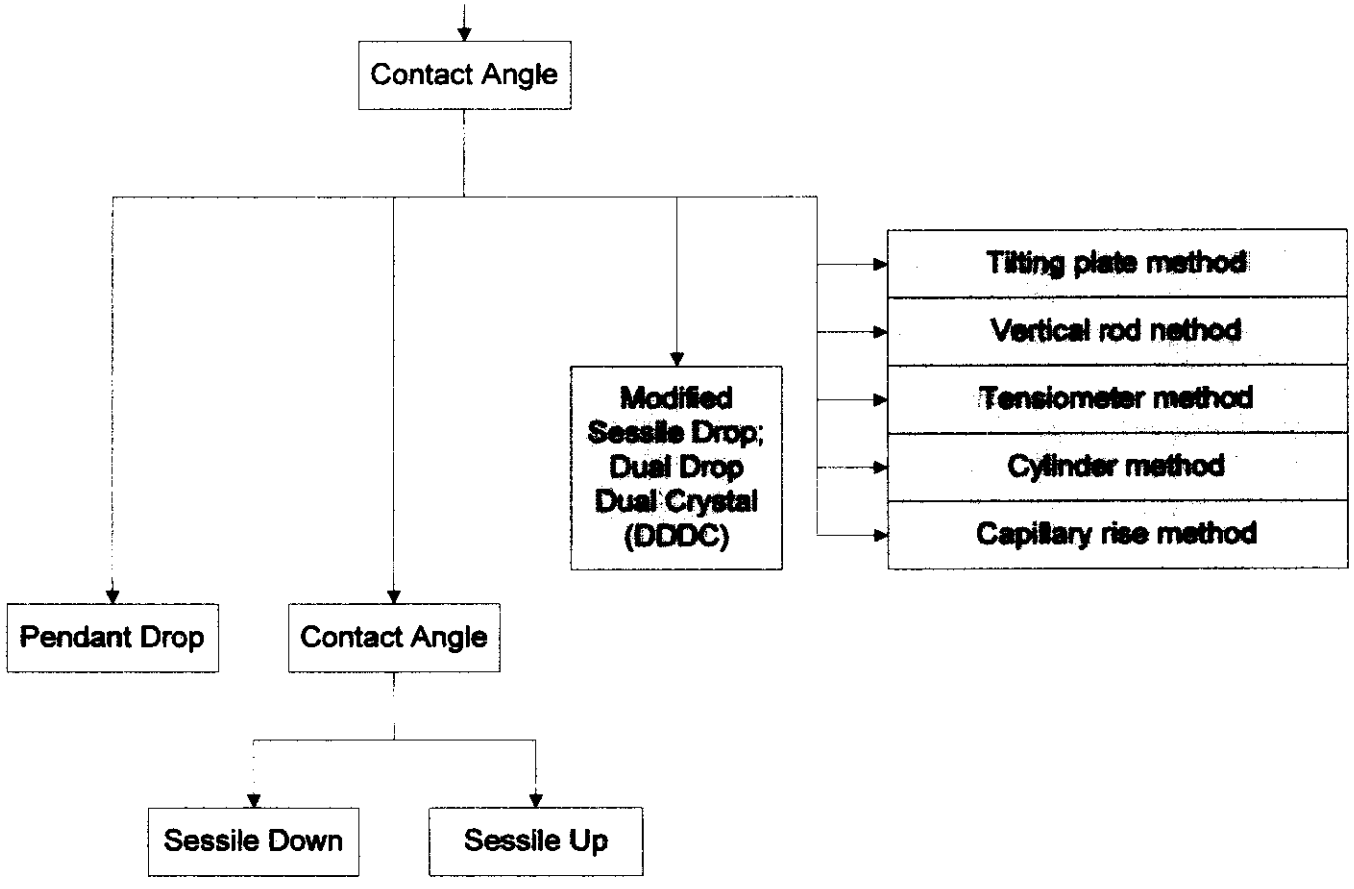


Figure 4. Wettability Measurement Technique Selection

3.4. Aging Time (duration to allow equilibrium for IFT and Contact Angle measurement)

M.B. Aloitabi and H.A. Nasr-El-Din (2009) summarized that the IFT is a dynamic property and time dependant [22]. Measurement of IFT are normally performed when the immicible fluids are assumed to be in equilibrium. As in the case of liquid-liquid-solid system, the equilibrium between the IFTs as shown in figure 2 will also enable the contact angle to be measured. In the summary, aging effect of IFT studies were presented as shown in table 6.

Table 6. Aging time studies for IFT measurement

Researchers	Fluids Tested for dynamic IFT	Concluded Time to Reach Equilibrium
Hassan et al (1953)	Propane, n-butane, n-pentane, n-hexane, n-octane, i-octane and benzene against water	2 minutes
Jasper et al (1970)	Benzene and water	5 minutes
McCaffery (1972)	n-dodecane and water	Decrease of less than 1 dyne/cm was noted after 15 seconds to 30 minutes of aging. The author concluded 10 minutes was sufficient for the aging drop to reach equilibrium.
Firoozabadi and Ramey (1988)	Three reservoir oil brine systems	Equilibrium ranged between 20 to 100 minutes
Xu (2005)	Live oil and formation brine at 82 deg F and 700 psi	Within the period of 10 days the author observed that most IFT decrease occur during the first hour and IFT equilibrium is reached at 4.5 hours. This is a very long time and uncommon for IFT measurement

3.5. Research Methodology

3.5.1. Brine Preparation

Four liters of brine of each surfactant concentrations are prepared by dissolving Sodium Chloride, NaCl and surfactant, Sodium Dodecyl Sulfate, $CH_3(CH_2)_{11}OSO_3Na$ in distilled water according to amounts specified in table below;

Table 7. Amount of Sodium Chloride, NaCl and surfactant, Sodium Dodecyl Sulfate, $CH_3(CH_2)_{11}OSO_3Na$ required to make brine

Surfactant Concentration, (ppm)	0	500	1500	3500	Total Amount
Sodium Dodecyl Sufate (g)	0	2	6	14	22
Sodium Chloride (g)	6	6	6	6	24

3.3.2. Core Properties Measurement

Surfactant	Oil	Core Properties				
		L(mm)	D(mm)	Kair(md)	K∞(md)	PHI(%)
Sodium Dodecyl Sufate	Baronia	76.15	38.37	208.755	197.176	20.138

Table 8. Core Properties

3.3.3. Core Slicing/Trimming

The core trimming device is used to cut the core sample into thin slices. Six slice were made to provide solid surfaces for the contact angle determination with oil bubble using sessile up orientation.

3.3.4. Contact Angle Measurement Procedure (Drop Shape Method)

Drop shape analysis is used to measure the contact angle. It also enable the determination of surface energy. The assumptions used for drop shape analysis are;

1) The drop is symetric about a central vertical axis. Thus it is irrelevant from which direction the drop is viewed because the shape will be the same.
2) The drop in static equilibrium is not affected by viscosity and inertia. Only interfacial tension and gravity forces acting on the motionless drop.

Optical magnification is required to enable contact angle measurements. The device, IFT 700 comes with a software equiped with the mathematical expression that can be fitted to the shape of the drop. It then calculate the tangent to the drop at the liquid-solid-vapor (LSV) interface line or liquid-liquid-solid (LLS) interface line, depending on the system tested.

Step 1: Determine Drop Orientation

There are two drop orientations for sessile method namely;

1) **Sessile down** or sessile drop. This orientation is selected from the user interface if **water drop is injected from the top** so that the water drop will sit on the core slice surrounded by oil.

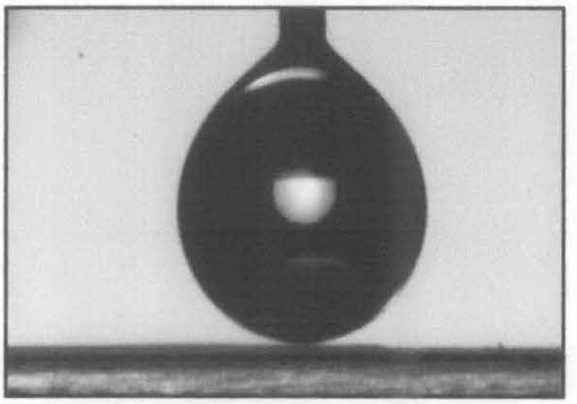


Figure 5a. Sessile down/ sessile drop, a drop is being released.

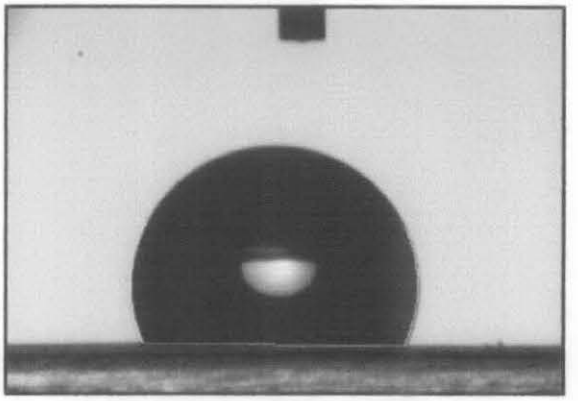


Figure 5b. Sessile down/ sessile drop, a drop lying on a solid sample.

2) **Sessile up** or sessile bubble. This orientation is selected from the user interface if **oil drop is injected from the bottom** so that the oil drop will float up in the brine and rest at the rock slice bottom.

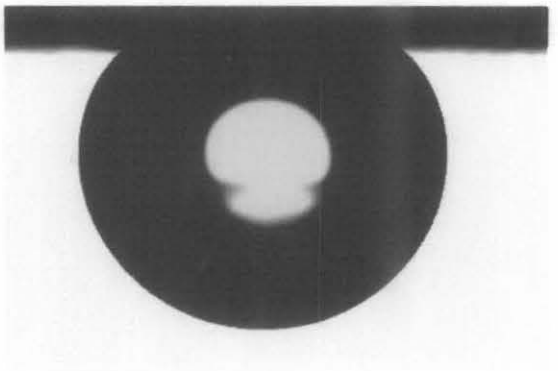


Figure 6. Sessile up/ sessile bubble, bubble sitting beneath solid surface captived by other immicible fluid

Since the back light is not bright enough to give us the view of the water drop surrounded by oil, the second orientation is selected.

Step 2: Instrument Setup

1) Core slice is mounted on a holder so it may be held in horizontal position. Double sided tape is used to place the core slice on the holder.
2) The core slice holder is placed in the core chamber.
3) Test fluids (oil and brine) are placed in syringes that will be attached to the inlet ports on the device, IFT 700. These ports are connected to the sample chamber through tubing lines.

Step 3: Fluid Loading

The software requires some external parameters to be supplied such as, needle size (internal/external diameter) and fluid densities.

4) Syringes are attached to the inlet ports.
5) Brine is fed into the chamber until it is full.

Step 4: Drop Dispense/Release

6) Oil drop is formed at the tip of the needle and released
7) Initial live video image of the sample is obtained. Camera focus is adjusted so that the tip of the needle image is visibly sharp. The camera viewing angle is adjusted so that the needle image is vertical on the computer screen. Camera focus is adjusted to get a clear image of the oil bubble at the bottom of core slice.

It is normal to test using oil and water first before the actual test fluids (oil and brine/surfactant) are used for contact angle and surface energy analysis.

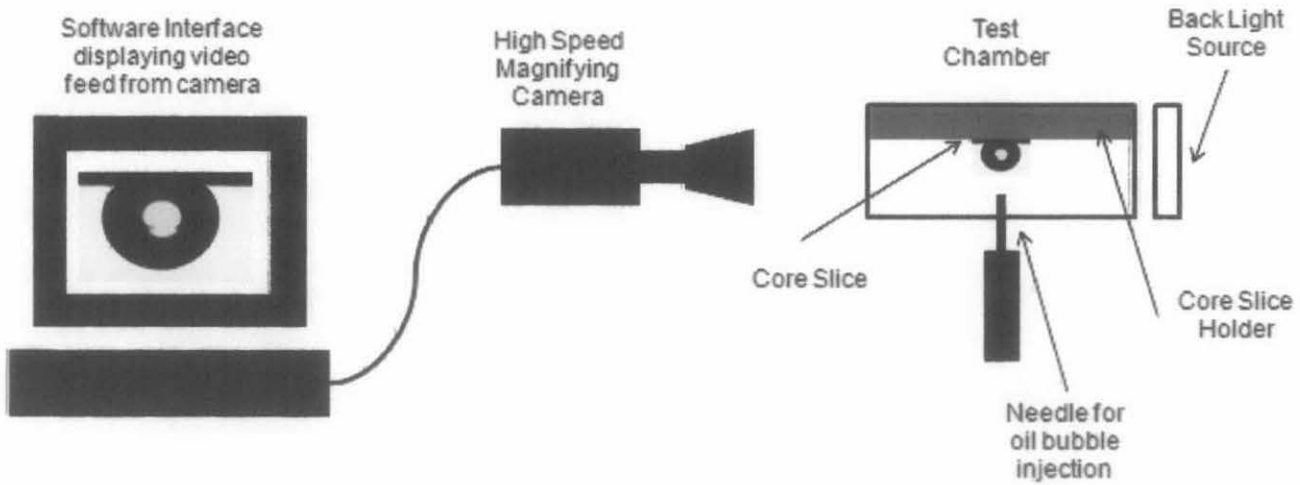


Figure 7. Simplified experimental setup for sessile up procedure

3.6. Key Milestone

Table 9. Key Milestone

Week (2010)		Milestone
1	Jan 25-Jan 31	•Request for chemicals (Sodium Chloride, Sodium Dodecyl Sulfate) approved by Chemical Engineering Lab Executive •Laboratory use for chemical solutions preparation application approved by Chemical Engineering Lab Executive
2	Feb 1-Feb 7	•Laboratory and devices use (Core Analysis Lab, IFT 700, poro-perm, oven, core trimmer, vacuum chamber) applicaation approved by Mechanical Engineering Lab Executive and Petroleum Engineering Department Technician
3	Feb 8-Feb 14	•Chemical preparation (brine solution, brine/SDS solution) completed
4	Feb 15-Feb 21	
5	Feb 22-Feb 28	•Core properties measurement (porosity, permeability) completed •Progress Report 1 submitted (Feb 25)
6	Mar 1-Mar 7	•Further literature review on IFT and Contact Angle research papers •Experimental Procedure determination and refinement
7	Mar 8-Mar 14	•Core trimming/ sclicing to get solid surfaces for contact angle measurement completed •Core slices saturation in brine/SDS commenced
8	Mar 15-Mar 21	•MID-SEM BREAK •Saturation of core slices continued
9	Mar 22-Mar 28	•Experimental setup/ mechanical concfiguration for sessile up on IFT 700 was arranged •A test run is performed to confirm the operability of the arrangement •Software measurement configuration was explored
10	Mar 29-April 4	•Experiment/ Test commenced •Maintenance is performed intermittenly
11	April 5-April 11	•Result analysis •Submission of Progress Report 2

3.7. Gantt Chart of Project Activities

Table 10. Gantt Chart of Project Activities

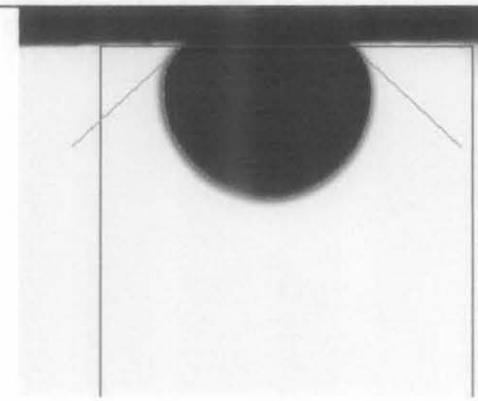
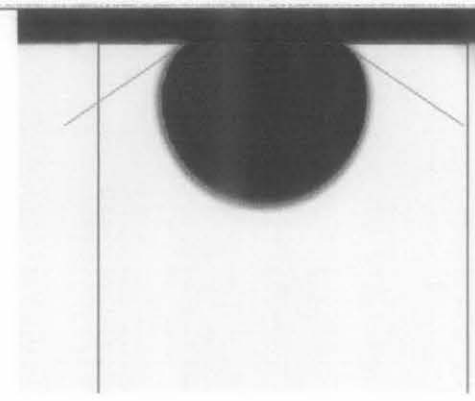
Week	1	2	3	4	5	6	7	8	9	10	11
Activity	Jan-25	Feb-01	Feb-08	Feb-15	Feb-22	Mar 1	Mar 8	Mar 15	Mar 22	Mar 29	Apr-05
• Request for chemicals (Sodium Chloride, Sodium Dodecyl Sulfate)											
• apply to use laboratory for chemical solutions preparation											
• Apply for laboratory and devices use (Core Analysis Lab, IFT 700, poro-perm, oven, core trimmer, vacuum chamber) through Mechanical Engineering Lab Executive and Petroleum Engineering Department Technician											
• Chemical preparation (brine solution, brine/SDS solution)											
• Core properties measurement (porosity, permeability)											
• Progress Report 1 submission (Feb 25)											
• Further literature review on IFT and Contact Angle research papers											
• Experimental Procedure determination and refinement											
• Core trimming/ sclicing to get solid surfaces for contact angle measurement											
• Commence core slices saturation in brine/SDS											
• MID-SEM BREAK											
• Continue saturation of core slices											
• Arrange experimental setup/ mechanical concfiguration for sessile up on IFT 700											
• Perform test run to confirm the operability of the arrangement											
• Explore software measurement configuration											
• Commence experiment/ Test											
• intermittent maintenance											
• Result analysis											
• Submission of Progress Report 2											

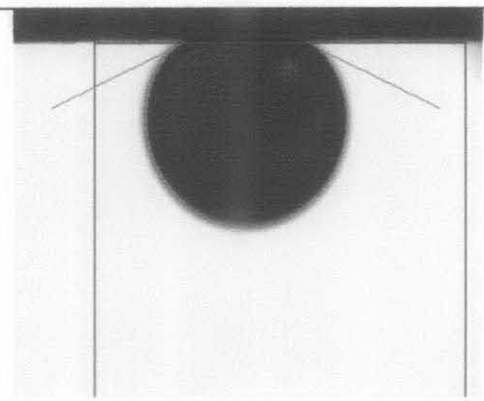
4. RESULT AND DISCUSSION

4.1. Expected Result

The purpose of using surfactant is to alter the wettability to more water wet. Increasing water wetness means contact angle will decrease with increasing concentration of surfactant. Visual inspection of images below (table 11) reveal the expected reduction in contact angles as surfactant concentration increases. Section 4.1.1. shows sample calculation of contact angle using these images.

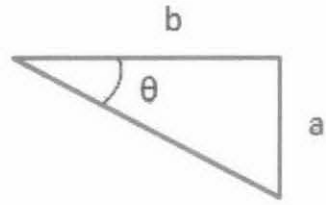
Table 11. Sample visual images of oil bubble for contact angle measurement

Surfactant Concentration, ppm	Image
0	
500	

1500	

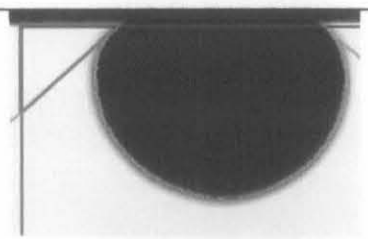
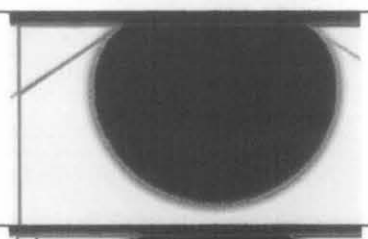
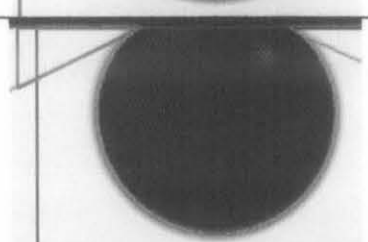
4.1.1. Contact Angle Calculation

Contact angle is calculated manually using simple trigonometri. For example;



Where angle θ, is obtained from the inverse of tangent **a** to **b, tan^{-}(a/b)**

Table 12. Contact angles (sample calculation) for various surfactant concentrations

SDS Concentration, ppm	Image	Ratio a/b	Inverse tangent, $\tan^{-1}(a/b)$	Contact Angle, θ
0		0.8333	39.81	39.81^{o}
500		0.6154	31.61	31.61^{o}
1500		0.4286	23.20	23.20^{o}

4.1.2. Wettability Determination

Table 12 shows the contact angles indeed decrease with increase surfactant concentration. As expected, higher surfactant concentrations increase the wettability to more water wet.

Contact angle is measured once the oil drop is in equilibrium with water, that is after the drop is in static condition. Once the equilibrium is achieved, the tensions, σ (as shown in figure 8 below) are also in equilibrium.

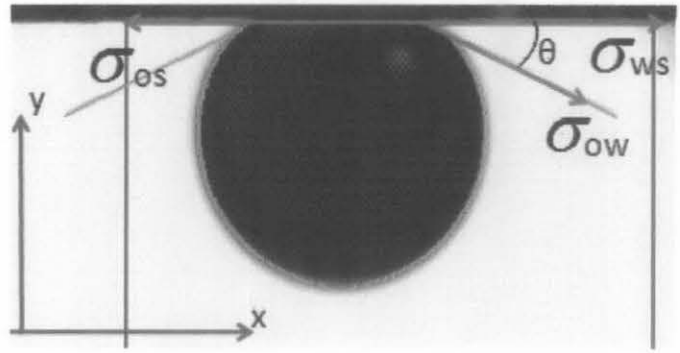


Figure 8. IFTs of oil-water-solid in equilibrium

At equilibrium, the net tension in the positive-x and negative-x direction must be equal. Thus;

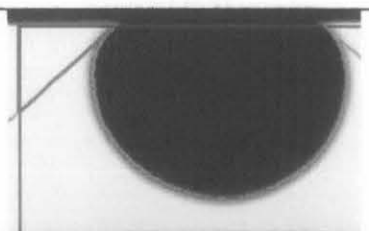
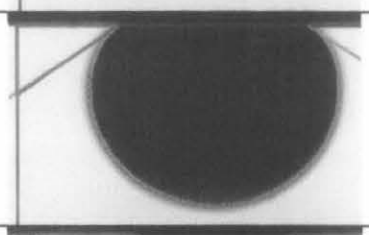
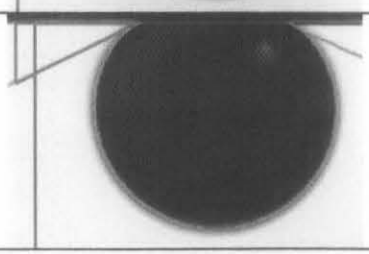
$$\sigma_{os} = \sigma_{ow} \cos\theta + \sigma_{ws}$$

Rearrange;

$$\cos\theta = (\sigma_{os} - \sigma_{ws}) / \sigma_{ow}$$

Water wet condition is when contact angle, θ is less than 90°. $\cos\theta$ for angles less than 90° are positive values. Thus a more positive value indicates a more water wet condition. Likewise, negative values for $\cos\theta$ (angle greater than 90°) indicate oil wet conditions. Using contact angles calculated from **table 12**, wettability is determined by calculating $\cos\theta$, as presented in **table 13**.

Table 13. Wettability determination from $\cos\theta$

SDS Concentration, ppm	Image	Contact Angle, θ	$\cos\theta$
0		39.81°	0.7682
500		31.61°	0.8516
1500		23.20°	0.9191

A graph of $\cos\theta$ vs surfactant concentration can be plot now.

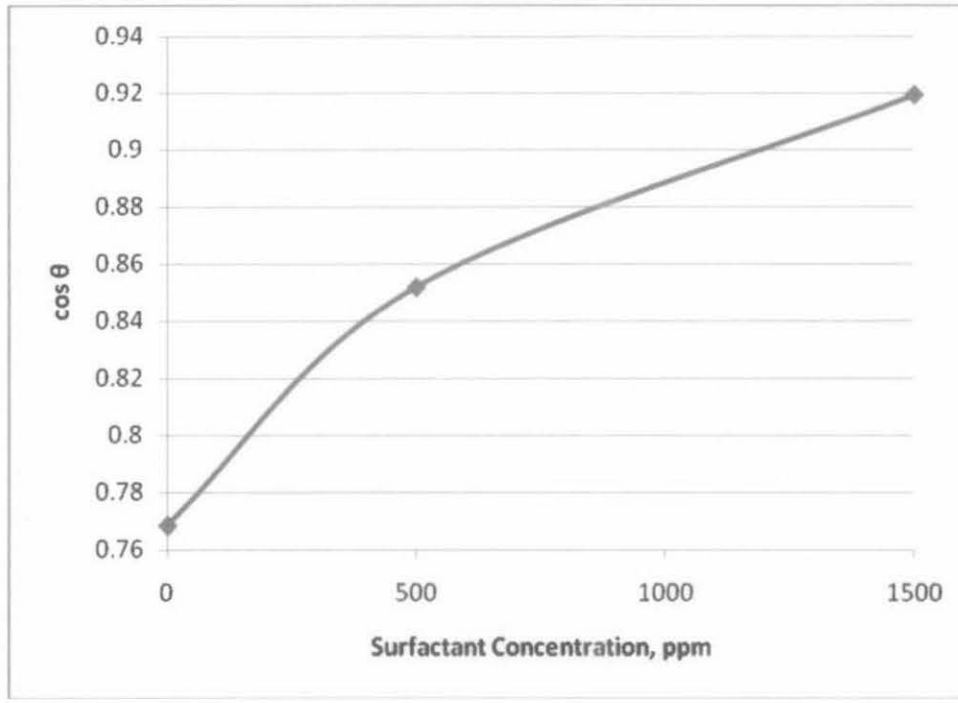


Figure 9. $\cos\theta$ vs surfactant concentration

The increasing trend of $\cos\theta$ as surfactant concentration increases is an indication of wettability becoming more water wet.

4.2. Actual Result

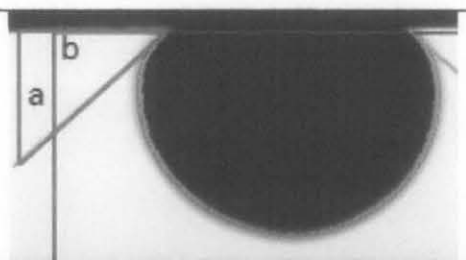
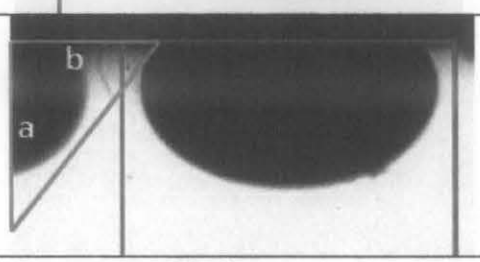
Before the contact angle is measured, core slices are saturated for 15 days in brine/SDS solutions with the aid of vacuum in the first three hours. Table 14 shows the core slices and the surfactant concentrations used for saturation. Table 15 shows the result of contact angle measurement tests.

Table 14. Core slice saturation with surfactant of different concentrations

Core Slice Number	Surfactant Concentration, ppm
1	0
2	500
3	1500

4.2.1. Contact Angle Calculation

Table 15. Result of contact angle measurement tests.

Test set	Core Slice	SDS concentration, ppm	Image	Ratio a/b	Inverse tangent, $\tan^{-}$ (a/b)	Contact angle, θ	$\cos\theta$
1	1	0		0.8500	40.36	40.36°	0.7620
2	2	500		1.3077	52.59	52.59°	0.6075
3	3	1500	No image				

4.2.2. Wettability Determination

The values of $\cos\theta$ as for both tests with surfactant of 0 ppm and 500ppm are positive (refer Table 15). This indicates the original wettability of the rock is water wet (0 ppm SDS test). This is not surprising since most sandstone reservoirs range from neutral to strongly water wet [35]. Figure 10 shows the plot of $\cos\theta$ vs surfactant concentration. The decreasing trend of $\cos\theta$ with increasing surfactant concentration indicates the wettability has become more oil wet or less water wet. This reverse wettability change effect in this test is discussed in the **Discussion section of 4.2.4.** The reason for unavaiability of image for test set 3 (1500 ppm surfactant) also can be found in the same section. Problems encountered while completing the tests is presented in the next section, **4.2.3.**

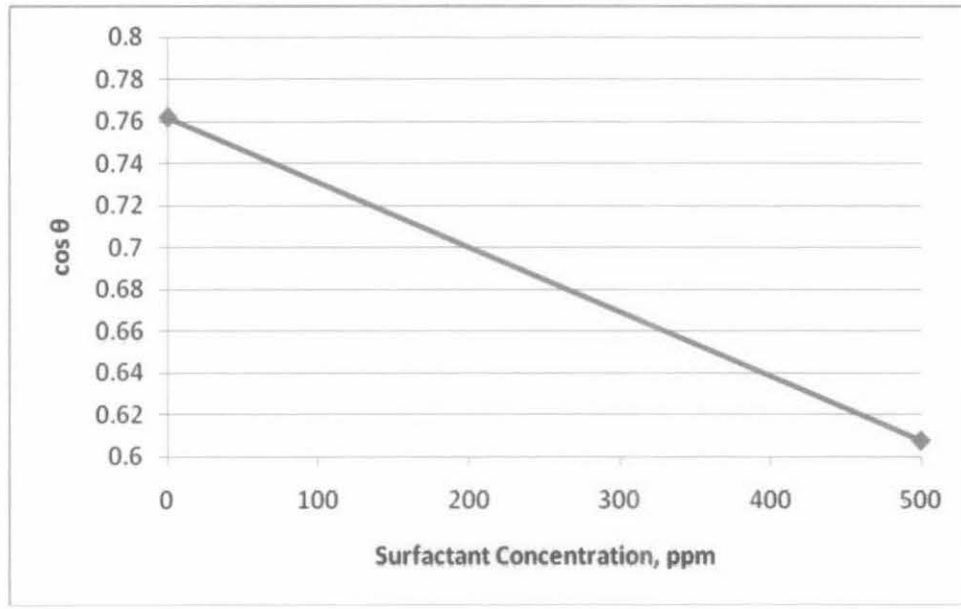


Figure 10. $\cos\theta$ vs surfactant concentration.

4.2.3. Problems Encountered in Completing the Tests

While performing the experiment,several problems are encountered and solved with the help of technician. Table 16.a. and 16.b. lists the type of problems and the occurence frequency.

Table 16.a. Mechanical problems

Type of failure		Cause	Effect	Action	Occurance frequency
Mechanical	Tubing joints leak	• Joint disconnected/ unconnected joint • Loose bolt and nut at tubing joint	• Brine level drop in the sample test chamber	• Refill brine/SDS in syringe • Pump brine/SDS into the test chamber again	Set1: 4x Set2: 5x Set3: 2x
	Pressure regulator malfunction	• Rubber ring within pressure regulator broke	• Brine/SDS cannot be pumped to fill up the test chamber	• Disassemble pressure regulator and replace the ring *(note:has to be done by the technician due to its complex mechanical nature)*	Set1: 1x Set2: 2x

Table 16.b. Operational problems.

Type of failure		Cause	Effect	Action	Occurance frequency
Operational	Air bubble trap in needle tip	• When the test chamber is being filled with brine/SDS, air within the needle is trapped	• Oil drop created contain smaller air bubble	• Create oil bubble at extremely slow rate, so that the oil bubble created is free from air bubble *(note: this will not always work)*	Set1: 1x Set2: 2x Set3: 2x
	Uneven slotting of core sample holder into test chamber	• After slot dislodging of core slice holder due to pressure increase in chamber during brine feed • There is no proper hook/connector to attach the holder in the chamber	• Need to drain the brine out of chamber and start over again • Oil bubble released from needle will not rest at point of touch with core slice, rather the bubble slides to the periphery of core slice (out of camera view) leaving no image of oil bubble to be analysed	• Double sided tape is used to keep the holder in place • Slotting holder using guide rod that is placed at the center of test chamber	Set1: 3x Set2: 4x Set3: 1x
	Over release of oil from needle	• Probably due to oil creation rate too high and/or preesure regulator failure	• Oil layer forms at the bottom surface of core slice, thus contaminating the sample	• Drain out the brine from test chamber and clean the core slice from oil stain and start over	Set2: 2x

4.2.4. Discussion

Table 17. Discussion

Test Set	1 (0 ppm)	2 (500 ppm)	3 (1500 ppm)
Video feed/image captured (refer table 15)	•Oil drop/ bubble image is sharp/ very clear •Base line image is also sharp •The sharp baseline enable the software to determine the tangent at base of oil bubble, thus contact angle can be calculated	•Oil drop/ bubble image is fair •Base line image is not sharp •The software is unable to determine the tangent at base line •However the tangent can still be located manually, thus enable contact angle determination	•No image of oil drop/bubble •Set 3 experienced problem of **uneven slotting of core sample holder into test chamber** (refer table 16.b) •This problem caused the oil bubles created to slide away from the center of camera view to the periphery of core slice beyong the camera view
Wettability	•Water wet •This is common for a sandstone reservoir	•Water wet •Test result shows that the degree of water wetness is reduced as compared to test set 1 •Test set 2 experienced **over release of oil from needle,** and **uneven slotting of core sample holder into test chamber** (refer table 16.b) resulting in oil layer formation at the exposed core slice surface •that contaminated the core slice surface and made the surface more oil wet	•No analysis •The fact that the oil bubbles created slide away and did not stick on the rock surface is an indication that the rock surface is very much water wet

4.3. Repeat Experiment Result

The contact angle measurement is performed again using new core slices obtained from the same Berea core sample. The experiment is performed with great care to minimize the problems encountered during the previous run.

Table 18 shows the core slices and the surfactant concentrations used for saturation. Table 19 shows the result of the repeat contact angle measurement tests.

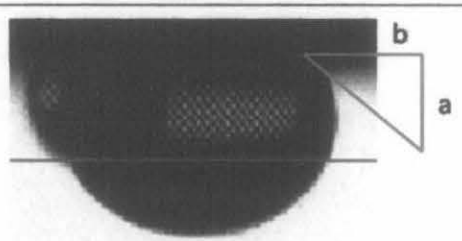
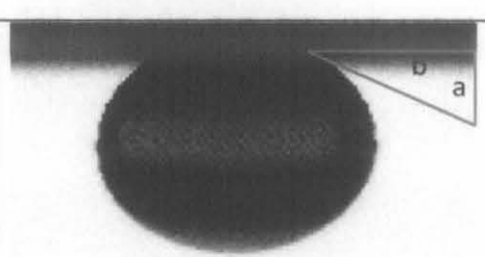
The only problem faced during this repeat test is the core slice holder dislodged after the chamber is filled with surfactant/brine of 500 ppm SDS once.

Table 18. Core slice saturation with surfactant of different concentrations

Core Slice Number	Surfactant Concentration, ppm
4	500
5	1500

4.3.1. Repeat Experiment Contact Angle Calculation

Table 19. Repeat experiment contact angle calculation.

Test set	Core Slice	SDS concentration, ppm	Image	Ratio a/b	Inverse tangent, $\tan^{-}$ (a/b)	Contact angle, θ	$\cos\theta$
4	4	500		0.8462	40.24	40.24°	0.7633
5	5	1500		0.4706	25.20	25.20°	0.9048

4.3.2. Repeat Experiment Wettability Determination

A plot of $\cos\theta$ vs surfactant concentration for the repeat experiment is shown in Figure 11. There is an increasing trend of $\cos\theta$ with increasing surfactant concentration indicating the surfactant has changed the wettability to a more water wet condition.

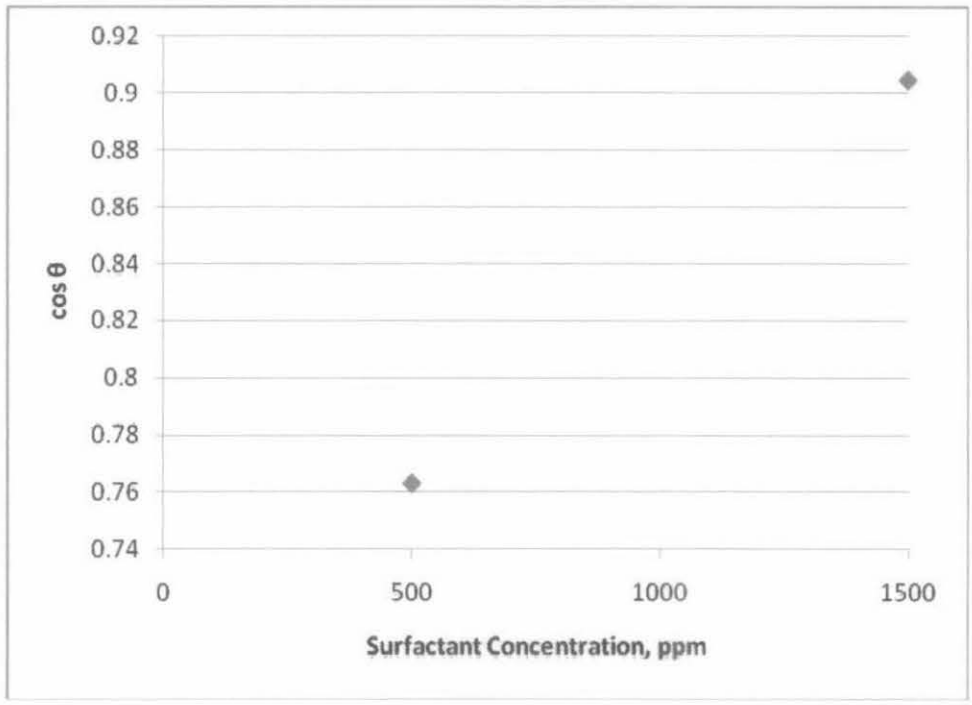


Figure 11. Repeat experiment $\cos\theta$ vs surfactant concentration.

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

The experimental result seems to suggest the wettability become less water wet as the concentration of surfactant increases. However, a better and more conclussive result could have been obtained if all the problems as shown in table 16a&b and section 4.2.3. can be reduced or eliminated. The elimination of those problems will significantly reduce the amount of time required to perform the test. Simplification of the mechanically complex device might resolve the pertinent problems in performing the sessile up experiment

Repeat Experiment

The repeat experiment was successfully completed with only one mechanical problem whereby the core slice holder dislodged from its place in the chamber. Unlike other problem it does not affect the wettability of the slice because the oil drop is not released yet. Therefore the result is more reliable and conclussive. The result suggest the surfactant works in improving the wettability to a more water wet condition.

5.2. Recommendations

5.2.1. Determine Wettability from Relative Permeability Curve Prior to Contact Angle Measurement

Many studies are performed and described in literatures over decades in order to determine the wettability from corefloods. The most widely derived parameters from such corefloods are relative permeabilies and until today they remains as the most important parameters that relate rock-fluids interactions in mathematical models developed to describe the reservoir flow phenomena [10]. Relative permeability is a parameter that combines the effects of several variables such as wettability, rock pore structure, fluid-fluid interfacial tension, fluid saturations, etc. Thus it is possible to perform an experimental procedure to

obtain relative permeability curves from the core samples before they are sliced to measure contact angle.

Many literatures regard contact angle measurement as a true universal measure of wettability. As mentioned earlier in the literature review section, contact angle is one of the quantitative measurements of wettability whereas deduction from relative permeability is a qualitative wettability determination. Wettability can be determined from relative permeability curve using Craig's rules of thumb. Dandina performed a study in order to find a correlation between wettability from corefloods and contact angle. The work described in SPE paper number 37234, "Is There a Correlation Between Wettability from Corefloods and Contact Angles?". Out of six systems studied, four rock-fluids systems yield similar wettability from both corefloods and contact angles.

As a recommendation for future works, one can emulate work done by Dandina N. Rao in which wettability determination from relative permeability curves are compared against wettability measurement from contact angle. Dandina recommended the contact angle is measured using the dual-drop-dual-crystal (DDDC) technique instead of the traditional methods like sesile drop method and modified sesile drop method. The traditional methods have been identified with reproducibility problems. Reproducibility problem is resolved with the use of DDDC method.

5.2.2. Measure Wettability using Amott and United States Bureau of Mines, USBM

Contact angle measures the wettability of a specific surface, while Amott and United States Bureau of Mines,USBM methods measure the average wettability of the core sample [21,26]. Both methods are widely used as industrial standards for comparing the wettability of core samples.

William G. Anderson [26] listed four problems of contact angle measurement;

1) Hysteresis
2) Questionable representation of results to the actual conditions. The contact angle cannot take into account the roughness, heterogeneity, and complex geometry of the reservoir rock.
3) The contact angle cannot take into account the heterogeneity of the rock surface.
4) Presence or absence of permanently attached organic coatings on reservoir rock cannot be determined.

Further elaboration on these limitations can be found in "Wettability Literature Survey

5.2.3. Study Wettability at Reservoir Conditions and Use Live Oil as well as Stock Tank Oil

M. B Alotaibi and H.A. Nasr-El-Din (2008) noted that "the variation of IFT or surface tension with temperature and pressure strongly influences the fluids movement in a reservoir, and therefore are fundamental to the understanding of the role of interfacial forces in oil recovery." [22]. A study on the behaviour of IFT between oil and formation brines under varying temperature and pressure will improve our knowledge on the subject which is currently not well understood [22].

W. Xu *et al.* (2005) quoted Anderson's summary on the effect of temperature on wettability [21]. Changing the temperature will result in two different effects that tend to make the core more water-wet as temperature increases;

1) Increase in temperature tends to increase the solubility of wettability altering compounds. Some compounds desorb from the surface as temperature increases.
2) IFT and contact angle measured through water decrease with temperature rise. Experimental studies using cleaned cores, mineral oil, and brine proved that cores get more water wet at higher temperature whether or not any compound adsorb or desorb.

W. Xu *et al.* (2005) studied the effect of surface active chemicals on oil-water interfacial tension (IFT) and wettability in crude oil-brine-rock systems at reservoir conditions as describe in **section 2.1** [21]. The study found that the dynamic oil-water IFT was found to be a strong function of oil composition, **temperature** and slight dependence on **pressure**. Significant difference between advancing contact angles of live oil (55^{o}) and stocktank oil (154^{o}) were observed. This suggest the importance of performing the measurement using live oil and at reservoir conditions to determine in-situ reservoir wettability.

5.2.4. To Test with Alkaline Surfactant to Generate Additional Surfactant from Reaction between Alkali and Natural Organic Acids in Crude Oil

Alkaline surfactant, AS solution flood is recognize as an effective EOR process [24]. Injection of AS solution into an acidic reservoir causes the IFT reduction and wettability alteration that contribute to flood performance [24]. The injected alkali will react with natural organic acids in the crude oil to generate in-situ surfactants. Together the generated and added surfactants reduce the IFT and alter the wettability.

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